Water-Gas Shift Membrane Reactor Studies

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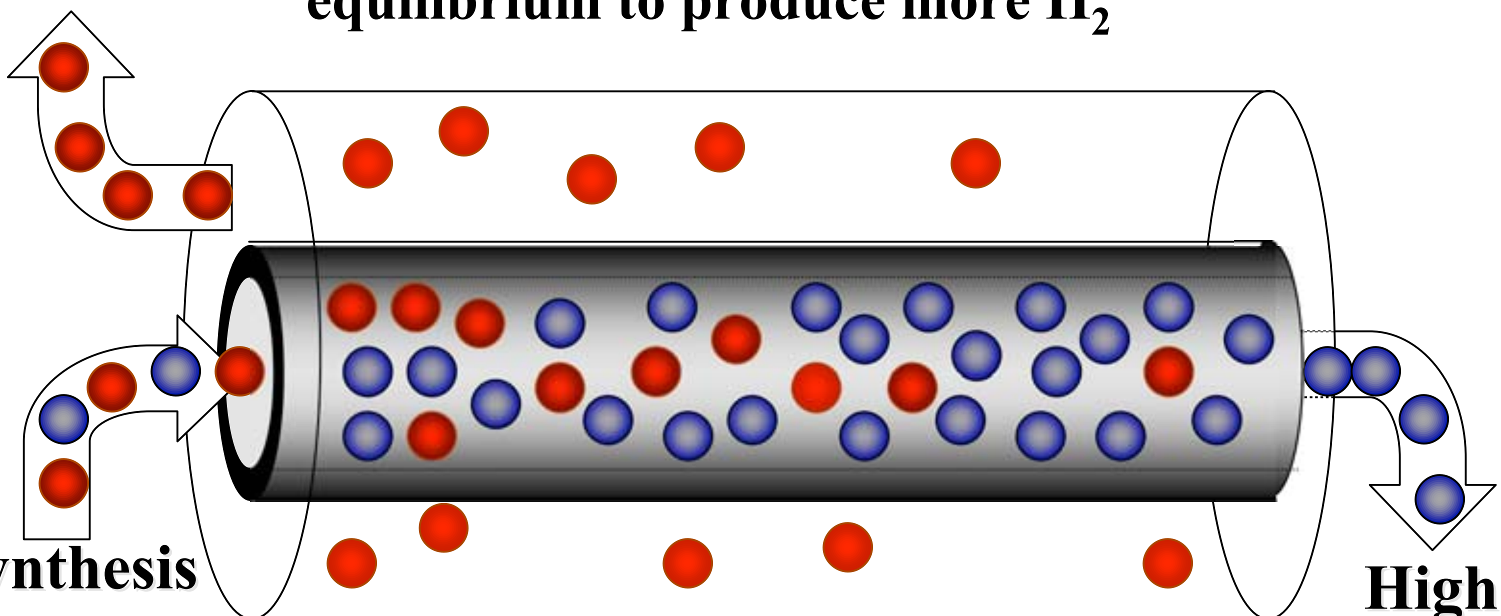
H_2 Membrane Reactor Concept

*WGS Reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$

*High-T for favorable kinetics

*Membrane removes H_2 to "shift" unfavorable equilibrium to produce more H_2



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Project Rationale

- **Designing WGS membrane reactors requires the consideration of reaction kinetics and mass transport phenomena**
  - Forward and Reverse Water-Gas Shift Kinetics
  - Catalytic Effect of Reactor Materials, Membrane Materials
  - Need for Heterogeneous Catalysis?
  - Hydrogen Flux and Selectivity Through Membrane
  - Durability of Membrane in Extreme Environments
- **Lab-scale approach**
  - Address scientific issues using mainly thick (i.e. 10's of microns), easy-to-manufacture membranes of precise composition
  - Incorporate the optimal alloy composition into membrane reactors of various geometries that have high flux with a highly permeable support

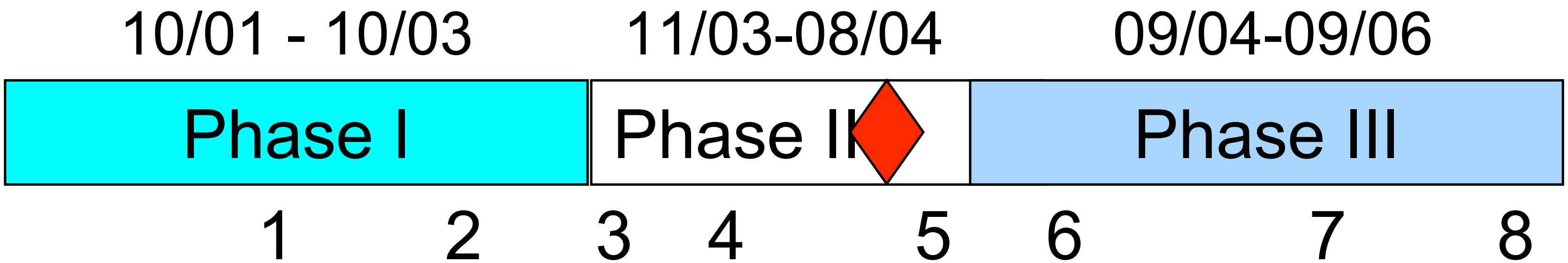
Objectives

- Evaluate water-gas shift (WGS) reaction kinetics and membrane flux using industrial gas mixtures and conditions
- Test the feasibility of enhancing the WGS <u>at high temperature without added catalyst particles</u> by using a membrane reactor
- Determine the catalytic effect of metal shell materials (e.g. Inconel) and membrane surfaces (e.g. Pd) on the WGS reaction

Budget

- Funding determined yearly thru submission of Annual Operating Plan proposals to EERE
- FY04 Funding = $200k
- EERE funding is 50% contribution to overall project; the other 50% is from FE

Project Timeline



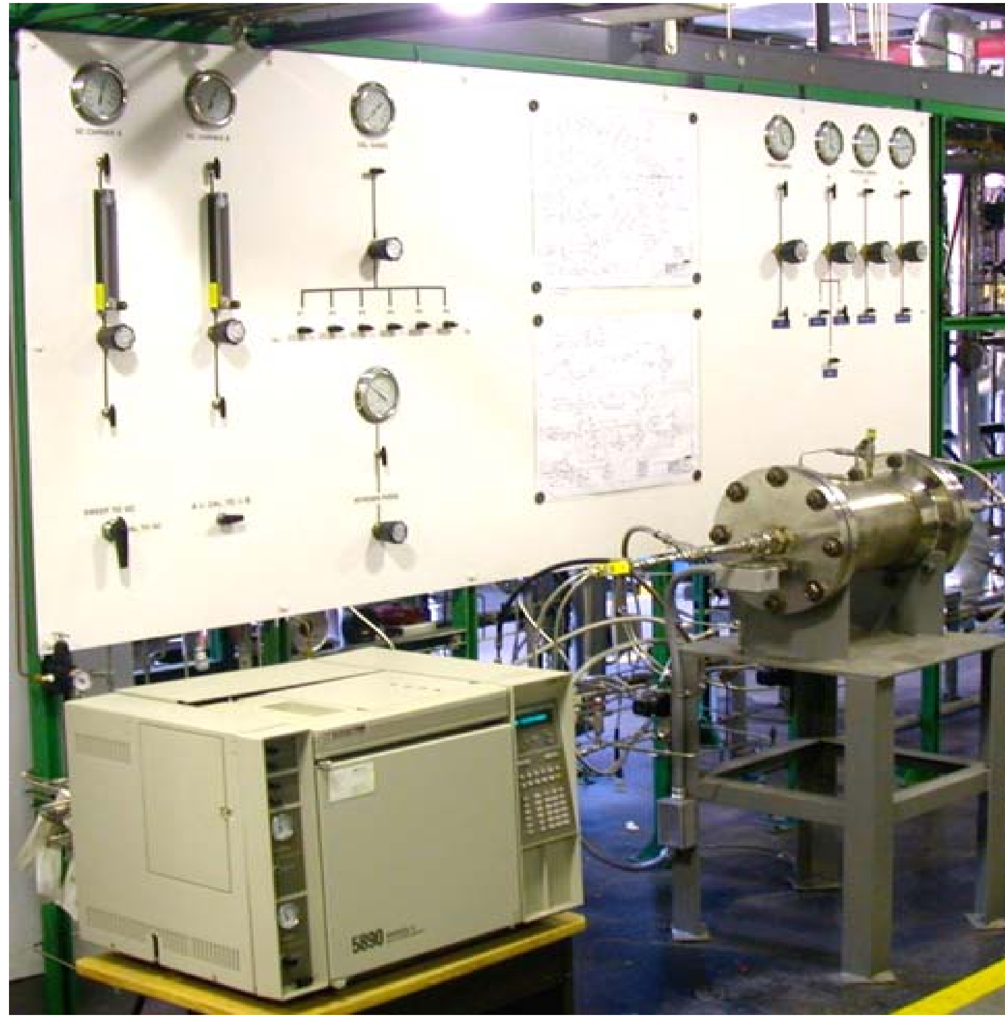
- **Phase I – Hi-T, Hi-P WGS Reaction Kinetics**
  1. Complete reverse WGS reaction kinetics study
  2. Complete forward WGS reaction kinetics study
  3. Determine catalytic effects of membrane/reactor materials
- **Phase II – Membrane Reactor Development**
  4. Fabricate different Pd membrane reactor prototypes
  5. Determine feasibility of Pd membrane reactor prototypes
- **Phase III – WGS Membrane Reactor Testing**
  6. Complete baseline testing of Pd-Cu membrane reactor
  7. Complete validation testing of optimized WGS MR system
  8. Operate WGS MR in presence of contaminants (e.g. H_2S)

Technical Barriers and Targets

- **Barrier A: Fuel Processor Capital Costs—specifically single-step shift w/integrated membrane technology**
  - Related 2005 Targets: Purification at a Cost of \$0.11/kg H_2 and H_2 Efficiency of 82%
- **Barrier AB: H_2 Separation & Purification—specifically membrane separation with the shift reaction in one unit operation**
  - Related 2005 Targets: Flux Rate of 100 scfh/ft^2, Cost of \$100-150/ft^2, Durability of 50,000 hours, Operating Temperature of 300-600°C, and Parasitic Power of 3.0 kWh/1000 scfh

NETL Hydrogen Separation Facilities

- **3 H_2 Membrane Test Units**
- **Constructed FY99 to FY02**
- **Temperatures to 900°C**
- **Pressures to 400 psi**
- **Disk & tubular membranes**
- **1/4” to 1/2” membranes**
- **Feed gas flexibility**
- **Membrane separation & reactor configurations**
- **“Clean” and “sulfur-laden” gas feedstocks**
- **Online analysis of products by GC**



Project Safety

- Safety vulnerability is addressed thru NETL's Safety Analysis & Review System (SARS). This process identifies, analyzes, minimizes all ES&H hazards. It ensures that all projects have a SARS Permit before operations begin.
- Management of changes is also addressed for any project or facility modifications thru the NETL SARS process.
- All H_2-related reactors are contained in purge vessels thru which an inert gas (N_2) is continually streaming.
- Gas alarm systems are in place in areas where gases such as H_2, H_2S, CO, CO_2, etc. are in use.

FY04 Approach

- Conduct baseline testing of the fWGS reaction at high pressure with no catalyst in the 300-900°C range in the prototype Pd & PdCu membrane reactors.

- Re-design the PdCu membrane reactor to maximize membrane area and minimize thickness in order to enhance conversions of CO and H_2O to H_2 and CO_2.

- Determine H_2 permeance of PdCu in the presence of major gasifier components, such as CO, H_2O, CO_2.

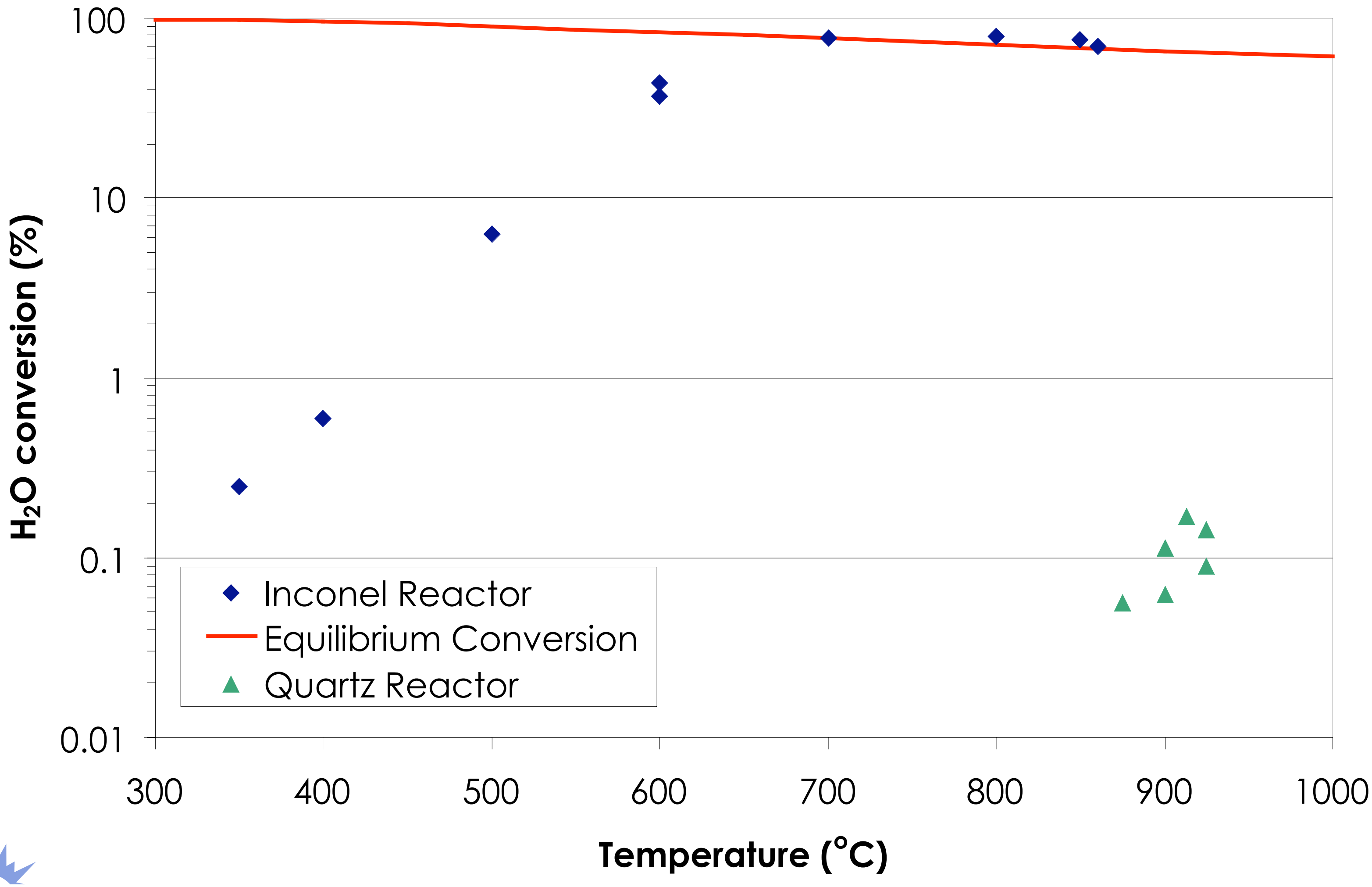
FY04 Accomplishments

- **Completed forward WGS kinetics study**
  - Gas phase kinetics
  - Correlation developed for high T, high P fWGS reaction
- **Determined catalytic effect of membrane and reactor shell materials**
  - Inconel – example of reactor shell material
  - Pd and Pd/Cu – examples of membrane materials
- **Evaluated effect of CO and H2O on H_2 permeability**
- **Fabricated 3 types of Pd MR for trials**
  - Pd flat disk in Inconel: assessment of effect of side reactions
  - Thin Pd tubes: effect of temperature, pressure, reactant ratio
- **Incorporated WGS kinetics results into MR model**

Forward WGS Kinetics

Inconel walls catalyze the reaction

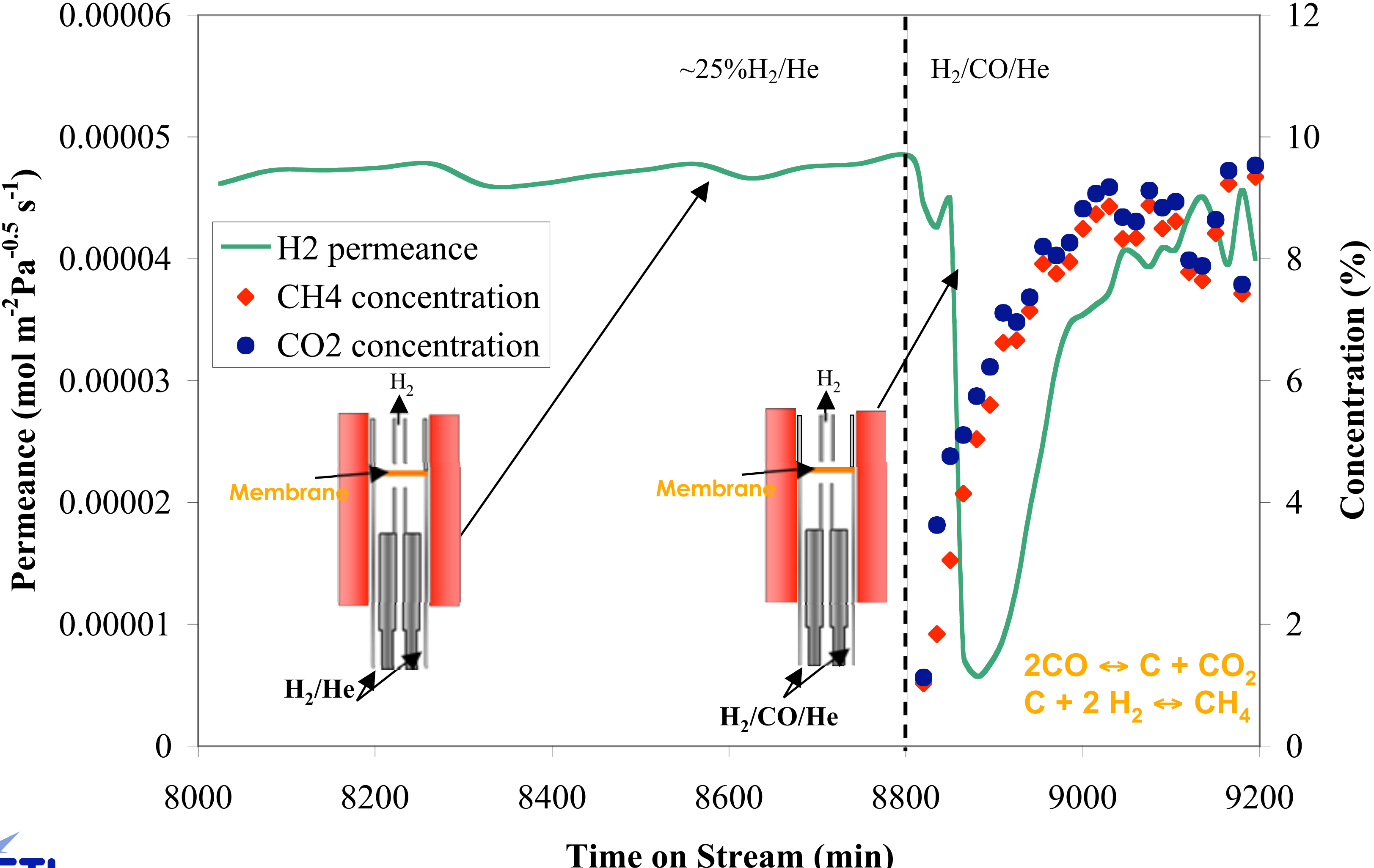
Gas-phase reaction appears to be slow



$(x_{CO})_0 = 0.72$, $(x_{H2O})_0 = 0.28$, $(x_{CO2})_0 = (x_{H2})_0$, $\tau \sim 0.5 - 1$ s

CO not a Poison for Pd Membranes at Hi-T

- *Physical, transient drop due to C deposition–permeability restored*
- *H_2O doesn't exert any effect on H_2 permeation (not shown)*



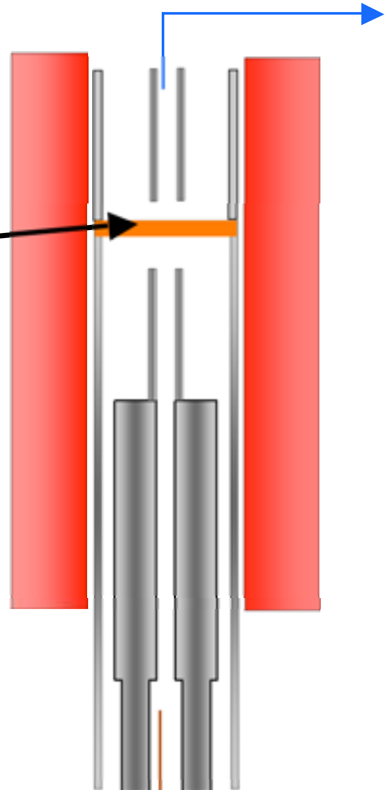
T = 900°C, Pretentate= 220 psig, Ppermeate= 5 psig, H_2/CO/He (~33% ea)

Inconel Enhances Kinetics & Pd Removes H_2

- *Good synergy between Inconel & Pd*
- *Side reactions on Inconel are significant*

H_2 removed by membrane* _ 24.2%

Pd Membrane



Conversions if only WGS in quartz reactor

CO _ 14.2 %
H2O _ 79.7 %

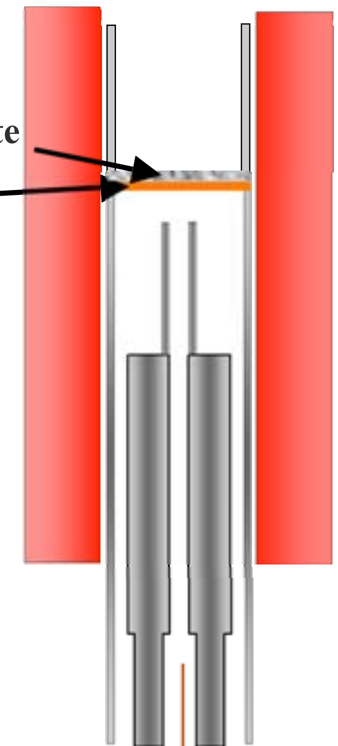
CO_2/H_2 = 5.84

<u>Conversions:</u>
CO _ 77.72 %
H_2O _ 66.25 %

Blank Reactor

Non-porous substrate

Thin Pd film



CO_2/H_2 = 4.10

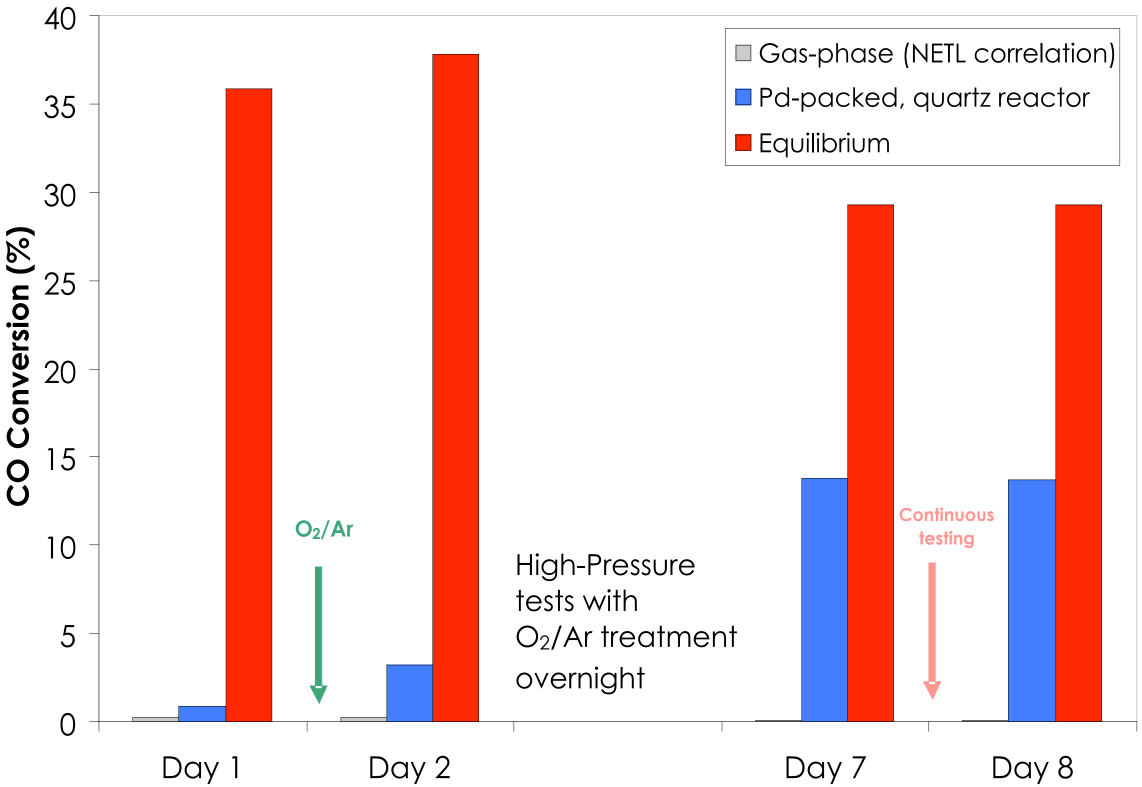
<u>Conversions:</u>
CO _ 77.16 %
H_2O _ 55.78 %

$$^*\left(\frac{F_{H_2,permeate}}{F_{H_2,permeate}+F_{H_2,retentate}}*100\right)$$

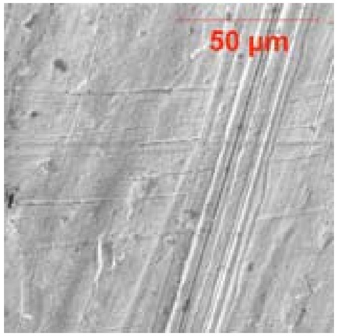
T = 900°C, P = 16 bar, τ = 2.5 s, $y_{CO,0}$ = 0.85, $y_{H2O,0}$ = 0.15

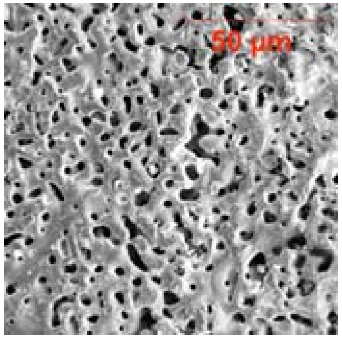
Pd or PdCu membrane surfaces enhance the WGS

- *Exposure of the Pd to O_2 to remove C roughens the membrane*
- *This increases surface area and enhances conversion activity,*
- *Need to operate at conditions where C deposits do not form*



SEM images of fresh (top) & oxidized (bottom) Pd packing shows increase in roughness; PdCu displays a similar behavior





$T = 900^oC$, $P = 1$ bar, $\tau = 0.7$ s, $y_{CO,0} = 0.70$, $y_{H2O,0} = 0.30$

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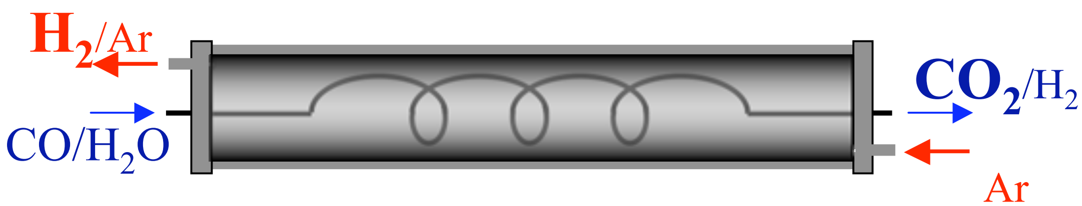
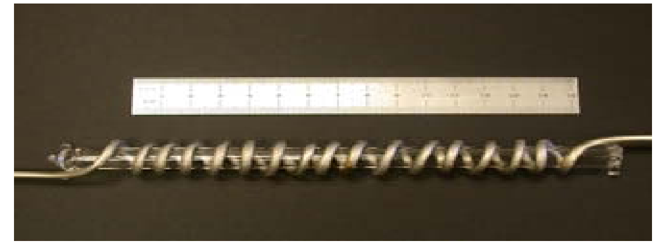
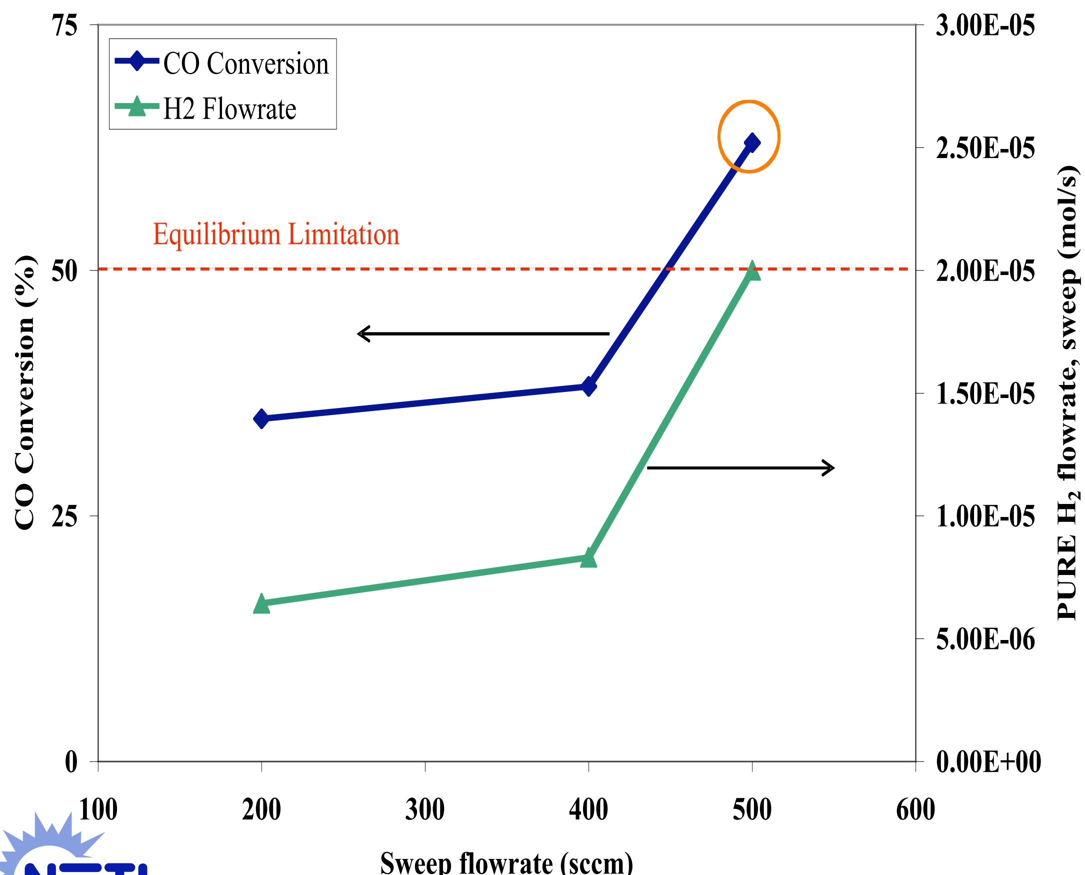
WGS Membrane Reactor Prototype







1) Helix design used to optimize surface-to-volume ratio
2) Graph shows CO conversions above equilibrium
3) In summary, WGS w/ membrane reactor yields more H2 than conventional WGSR at hi-temperature

Interactions, Collaborations, Papers

- Synetix (Johnson-Matthey) in the UK: Dr. Jim Abbott – informal exchange of WGS information
- Princeton Environmental Institute: Dr. Tom Kreutz – membrane reactor systems analyses
- Collaborations with ultra-thin Pd/Cu membrane developers: Dr. Doug Way (Pd/Cu/porous ceramic), Dr. Robert Buxbaum (Pd/Cu/dense metals), and Dr. Ed Ma (Pd/Cu/porous SS)

- F. Bustamante et al., "Hi-T, Hi-P WGS Reaction in a Membrane Reactor," AIChE Mtg., San Francisco, 11/03
- R. Enick et al., "Towards the Development of Robust Water-Gas Shift Reactors," ACS Mtg., New York, 8/03
- F. Bustamante et al., "Hi-T Kinetics of the Homogeneous rWGS Reaction," AIChE Journal, 05/04
- M. Ciocco et al., "Conducting the Hi-T&P WGSR in a Pd Membrane Reactor," Coal Util. Conf., Clearwater FL, 04/04

Responses to Reviewers' Comments Last Year

- Summary Comment — "emphasize feasibility of hi-temp WGS under realistic operating conditions"
- Response — project focus has shifted from kinetics studies to actual WGS membrane reactor testing using syngas components, reactor materials, high T&P, novel reactor designs

- No weaknesses specified in reviewers comments

Future Plans

- **FY04**
  - Conduct baseline testing of Pd membrane reactor (MR) to determine feasibility of prototype design
  - Fabricate Pd-Cu MR based on results of Pd testing and begin baseline testing
- **FY05**
  - Complete baseline testing of Pd-Cu MR
  - Determine effect of syngas components and impurities (S, Cl, NH3, etc.) on WGS MR
  - Complete initial validation tests under gasification conditions